Technical Report No. 6302

EVALUATION OF ADIPRENE L-100 URETHANE RUBBER AS A COSMETIC GLOVE MATERIAL

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Recommend Approval:

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Scientific Director

Approved:

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Director

*Qualified requesters may obtain copies of this report from ASTIA.

A B S T R A C T

Urethane rubber Adiprene L-100 was evaluated, using a polyol cure system, as a possible cosmetic glove material. It was found to have excellent flexibility and elastic properties but poor stain resistance, and processing difficulties further impair its usefulness as a substitute for vinyl plastisols in glove manufacture.

I. Introduction

Adiprene L-100 (formerly called Adiprene L), a product of Elastomer Chemicals Department, E. I. du Pont de Nemours & Co., is a liquid urethane polymer which can be cured to a strong, rubbery solid. Many curing systems are available. From a study of the manufacturer's literature it was determined that a polyol curing system would produce a cured film with the most likely properties for cosmetic glove application. Films were cast using 1,4-Butanediol and Trimethylolpropane as curing agents, and physical properties were determined. This report is concerned with the evaluation of this material for possible cosmetic glove use.

II. Processing

The formulation used to prepare the samples evaluated herein is as follows:

Adiprene L-100	100 gms.
1,4-Butanediol	3.2
Trimethylolpropane	0.9

In this system, the diol causes chain extension and the triol cross links the polymer.

The polyurethane polymer in its liquid, uncured state is very susceptible to attack by atmospheric moisture. In fact the material may be cured by exposing it to 50 percent humidity at 75°F, producing a rubber with tensile strength in the range of 4000 psi. Thus it is important to prevent any prolonged contact of the resin with air during the mixing of the components. Two alternative small batch mixing procedures are recommended by the manufacturer. Both of these were tried.

The first films cast were mixed in accordance with the method of P. E. Weiner (2). The 1,4-Butanediol was dried for two hours at 100°C and evacuated for one hour while hot. All

ingredients were preheated to 100°C and mixed together in a stainless steel beaker for three minutes. The mix was then evacuated for 20 minutes. A film was cast on a polished aluminum block which had been preheated to 140°C. The film was drawn down to a uniform thickness and cured for six hours at 140°C.

In the first attempt to cast a film, the cured polymer adhered so strongly to the block that it was impossible to remove the film intact. After this, the block was coated with a fluoro-carbon mold release (Miller-Stephenson S-122) which proved quite satisfactory, but it gave a "sandblasted" appearance to the otherwise clear film.

One batch of the urethane was made according to the method of R. J. Athey, et. al. (1). The equipment is shown in figure I. The procedure was as follows:

1. Dry 1,4-Butanediol in 100°C oven and evacuate.
2. Weigh out curing agents and heat to 100°C.
3. Weigh out resin into flask.
4. Heat resin to 100°C and evacuate.
5. Add curing agents and mix for three minutes under vacuum.
6. Cast film on preheated slab coated with mold release. Draw down to .050 inch thickness.
7. Cast remainder of resin-alcohol mixture in aluminum weighing dishes.
8. Cure all samples for six hours at 140°C.

III. Physical Properties

The following physical properties were obtained from films cast in the manner described above:

1. Tensile strength, ultimate elongation and modulus (tensile stress) at 100 and 300 percent elongation (ASTM D 412-51T) using the Instron tension testing machine.

2. Tear resistance (ASTM D 624-54) with the Instron machine.

3. Low temperature stiffness (ASTM D 747-58T) using the Tinius-Olsen stiffness tester in a refrigerated atmosphere at 10 degree intervals from -40° to +10°C.

4. Stain resistance, using the techniques of Mr. James Hill, in APRL Technical Reports 6202, 5904, 5903, and 5838. The vinyl cleaning solution (equal parts of MEK, Isopropanol and Trichloroethylene) was used.

The tensile properties of the material mixed according to the simplified procedure of Weiner were lower than those obtained using the vacuum equipment shown in figure I. This latter procedure corresponds more nearly to the commercial method, and the physical properties reported in table I at the end of this report, are those obtained using the vacuum mixing procedure.

IV. Color

All samples were quite transparent except for the sand-blasted effect imparted by the mold release, but the color of this material in its cured form was decidedly yellow. The resin itself has a color approximately that of honey, but the curing process darkens the material considerably. The color readings on the Gardner Color Difference Meter were as follows:

R_d	a	b	L
65.4	-0.8	+31.8	78.2

These readings were taken using the standard white tile with an R_d value of 88.9 and using the 1-inch opening and

condensing lenses. A slice was taken out of one of the samples cast in a weighing dish, and it was apparent that the dark color was concentrated in the open top of the film, i.e. that portion which was in contact with the air during curing. The rest of the sample, even that which came in contact with the mold, appeared water white. It was not possible to cut a sample large enough to take color readings.

A sample of the cured film was subjected to the ultra-violet lamp for a period of 35 days (ASTM D 620-57T). The film became considerably darker. The readings on the color difference meter were:

R_d	a	b	L
50.4	+7.0	+35.5	70.0

One of the slices cut from the aluminum disk specimen was also subjected to the ultra-violet treatment. It darkened to some extent, but did not attain the color of the film exposed to air during cure. The sample was not large enough to take a quantitative measure of the extent of color change.

V. Discussion

1. Processing. There are many difficulties involved in the processing of Adiprene L-100 Urethane Rubber that are not encountered in the casting of gloves from poly (vinyl chloride) plastisols. The resin must be stored and processed in the absence of moisture. Mold releases must be employed, and cleaning of equipment becomes more difficult since the cured polymer adheres well even to quite smooth surfaces and is resistant to common solvents. Cure time is six hours as compared to twenty minutes for PVC plastisols.

In addition, this resin cannot be cast in a slush molding or rotational process such as is used in the casting of vinyl plastisols. An injection or transfer molding process would have to be employed using a complicated split mold. The material

has a pot life of only thirty minutes, and the polymer must be cured for thirty minutes before it has attained sufficient strength to be removed from the mold. Thus it would be necessary to mix the resin and curing agents in small quantities, or to have a large investment in molding equipment in order to manufacture several gloves from one batch of mix. It might be feasible to employ a mixing machine similar to those used in producing polyurethane foams. This would enable the processor to manufacture a small number of gloves without having to mix several small batches. (3)

Alternately, it may be possible to develop a means of casting gloves on a positive mold using a volatile solvent with a dipping or spraying technique. The gloves could then be turned inside out. But there is no apparent method of glove manufacture from a material of this type that does not involve a radical changeover in processing equipment, including the scrapping of the present molds.

2. Physical properties. As can be seen from the data of table I, the tensile strength of this material is more than adequate being in the upper range of that obtained from standard vinyl compositions. The modulus and low temperature flexibility are excellent; a glove would probably be operable at -40°C. The tear resistance is on the low side but still acceptable. However, the stain resistance of this material is too low to be accepted for use in cosmetic gloves. Such being the case, the urethane film discussed herein could only be used as a substrate - either as the inner layer of a dilaminar glove or when coated with some stain-resistant material.

3. Color. As noted, the cured film has a definite yellow-to-orange color. This color is too deep to be overcome by compensating for it in the painting of the glove by ordinary techniques. It would be necessary to paint the glove on the outside with opaque pigments.

Since it has been shown, however, that the dark color appears only on the outside (air-exposed) surface of the film or molded article, it is reasonable to expect that this problem

can be overcome by curing either in a closed mold or in the absence of air (in vacuum or perhaps in a nitrogen atmosphere). This represents yet another processing expense.

Color degradation under ultra-violet light will be a problem even if the dark color caused by curing in the presence of air is eliminated. If the glove is to be painted on the inside, exposure to sunlight will cause a gradual darkening in color. The writer has no knowledge of any light stabilizers that can be incorporated into this material.

4. Other curing systems. Adiprene L-100 can be cured by the use of 4,4'-Methylene-bis-(2-chloroaniline) to produce a rubber with excellent tensile strength, but the manufacturer's data indicate that the modulus (tensile stress) of this cured rubber would be over 2,000 psi at 300 per cent elongation. This is an indication of lack of that extensibility essential in a cosmetic glove. The modulus at 300% elongation of a rubber cured by atmospheric moisture is reported as 1,175 psi. (1).

VI. Conclusions

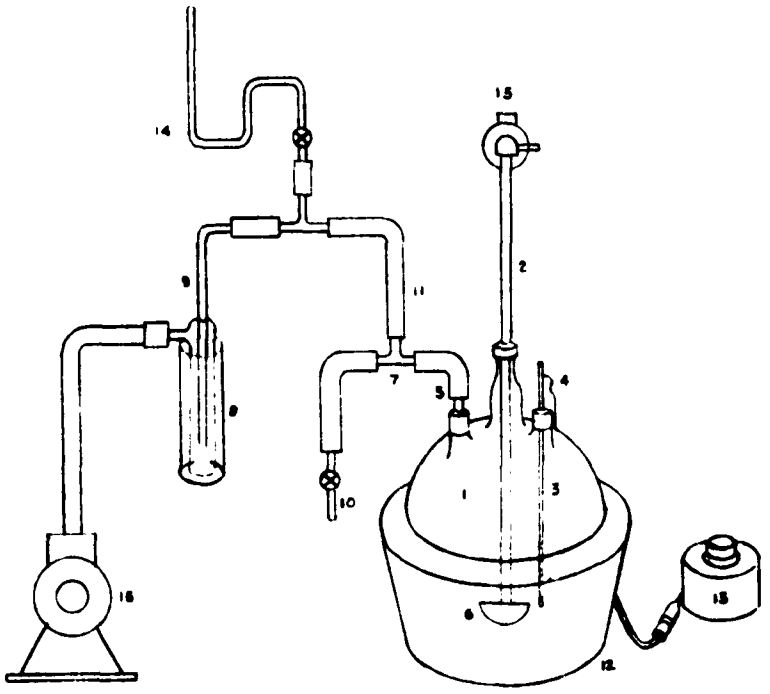
1. Adiprene L-100 cured with 1,4-Butanediol and Trimethylopropane produces a film with excellent flexibility and elasticity. Stain resistance, however, is very low and tear strength is barely acceptable.

2. Processing difficulties encountered in the manufacture of cosmetic gloves from this urethane system tend to make it economically unfeasible as a commercial process.

3. Other curing systems for this resin would entail the same processing difficulties, and manufacturer's data indicate that the modulus, which is an inverse measure of extensibility, would be too high in any case for cosmetic glove use.

ADIPRENE L BATCH

EQUIPMENT ARRANGEMENT



1. RESIN FLASK (4-necked)
2. STIRRER ASSEMBLY
3. THERMOMETER
4. STOPPER
5. ADAPTERS
6. TEFLON BLADE
7. CONNECTING TUBES
8. VACUUM FLASK
9. VAPOR TRAP
10. VACUUM RELEASE VALVE
11. RUBBER TUBING
12. HEATER (Glas-Col)
13. VARIAC
14. VACUUM GAUGE
15. STIRRING MOTOR
16. VACUUM PUMP

FIGURE I

TABLE I - Physical Properties of the Cured Film

Tensile Strength	2,130 psi
Ultimate elongation	520 %
Modulus (stress) 100%	210 psi
" 300%	377 psi
Tear Resistance	123 p/i
Stain resistance	35 %

Low temperature stiffness in flexure

Temperature °C	-40	-30	-20	-10	0	+10
Stiffness, psi	1,400	560	440	370	150	210

These properties were taken after aging the film for 14 days at room temperature. The standard vinyl cleaning solution (equal parts MEK, Isopropanol and Trichloroethylene) was used in the stain-resistance determination.

References

1. Athey, DePinto and Rugg, "Adiprene L, a Liquid Urethane Elastomer", March 1958, Elastomer Chemicals Department, E. I. du Pont de Nemours & Co., Wilmington, Delaware.

2. Weiner, P. E., "Small Scale Batch Mixing of Liquid Adiprene Polymers," June 1962, Elastomer Chemicals Department, E. I. du Pont de Nemours & Co., Wilmington, Delaware.

3. Society of the Plastics Industry, Inc., "Plastics Engineering Handbook," 1960, Reinhold Publishing Corporation, New York, New York.

4. USAPRL Research Notebook No. 201, pp. 84-92.

Acknowledgment

I wish to thank Mr. Donald Ingenito and the other members of the Resin Laboratory staff for their help in setting up the equipment in which this material was prepared.

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